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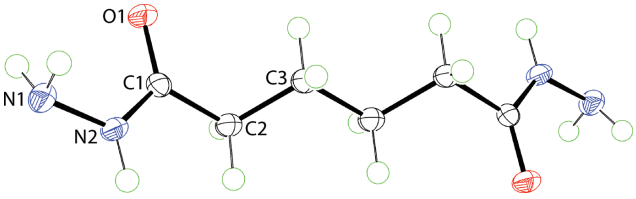
Kong Mun Lo, See Mun Lee and Edward R.T. Tiekink*

Crystal structure of hexanedihydrazide, $C_6H_{14}N_4O_2$



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Abstract

$C_6H_{14}N_4O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 12.2878(3)$ Å, $b = 4.8442(1)$ Å, $c = 7.0931(1)$ Å, $\beta = 97.546(2)°$, $V = 418.557(15)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0290$, $wR_{ref}(F^2) = 0.0829$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The crystals of the title compound were the unreacted adipic acid dihydrazide obtained from the reaction of adipic acid dihydrazide (Sigma-Aldrich, 0.17 g, 1 mmol) with 4-hydroxysalicylaldehyde (Merck, 0.27 g, 2.0 mmol) in ethanol (30 mL).

Yield: 0.03 g (17%). **M.pt** (Mel-temp II digital melting point apparatus): 452–454 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 3376 (br) ν(OH) & ν(NH), 1728(s) ν(C=O), 1653(m) ν(C=N), 1465(m) ν(C—O), 1089 (m) ν(N—N). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me_4Si, DMSO-d_6 solution at 40 °C; ppm): 1.56–1.57 (m, 4H, CH_2), 2.05–2.06 (m, 4H, CH_2), 4.05 (s, 4H, NH_2), 8.97 (s, 2H, NH). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 24.4 (CH_2), 34.1 (CH_2CO), 172.6 (CN).

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.12 × 0.09 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	0.88 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9520, 747, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 692
$N(param)_{refined}$:	65
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.22676(7)	0.82232(18)	0.39671(13)	0.0171(3)
N1	0.07234(9)	0.4738(2)	0.20003(16)	0.0162(3)
H1N	0.0913(13)	0.543(3)	0.0930(16)	0.019*
H2N	0.0446(12)	0.614(3)	0.258(2)	0.019*
N2	0.17031(9)	0.3906(2)	0.31416(15)	0.0147(3)
H3N	0.1830(13)	0.213(2)	0.326(2)	0.018*
C1	0.24186(10)	0.5696(3)	0.40318(17)	0.0128(3)
C2	0.34380(10)	0.4456(3)	0.51277(18)	0.0139(3)
H2A	0.341970	0.242617	0.496574	0.017*
H2B	0.344997	0.486234	0.649818	0.017*
C3	0.44803(10)	0.5601(3)	0.44510(17)	0.0143(3)
H3A	0.446770	0.518220	0.308222	0.017*
H3B	0.449129	0.763354	0.459953	0.017*

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H atoms were refined with N—H = 0.88 ± 0.01 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$. A correction for secondary extinction was made [coefficient = 0.0089(16)].

Comment

The title compound, $H_2NN(H)C(=O)(CH_2)_4C(=O)N(H)NH_2$, commonly known as adipic acid dihydrazide (ADH; alternative name: adipohydrazide), is a widely used, water-soluble chemical for cross-linking of species such as chitosan oligomers [5] and lipid-polymer hybrid nanoparticles for drug delivery [6]. Despite the wide use of ADH, no crystal structure determination has yet been reported for this molecule. Indeed, the only crystal structure containing ADH

***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my
Kong Mun Lo and See Mun Lee: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

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is that of a one-dimensional coordination polymer with a ladder topology, i.e. $[Zn_2(ADH)_3]_n \cdot 4n(NO_3)_2 \cdot 2nDMF$, where the octahedrally coordinated Zn atoms are chelated by the carbonyl-O and hydrazide-N atoms of each end of a bridging ADH molecule to form a five-membered ring [7]. In the present study, crystals of ADH, (I), became available during the reaction of adipic acid dihydrazide with 4-hydroxysalicylaldehyde.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) $1 - x$, $1 - y$, $1 - z$). The molecule is disposed around a centre of inversion with the C-backbone having an all-trans (+ anti-periplanar) conformation as seen in the values of the C1—C2—C3—$C3^i$ = 179.48(12)° and C2—C3—$C3^i$—$C2^i$ = 180°, from symmetry, torsion angles. A kink in the molecule is noted about the C1—C2 bond, i.e. the N2—C1—C2—C3 torsion angle = 122.88(12)°, indicating an + anti-clinal conformation. The key geometric parameters are N1—N2 = 1.4181(15) Å, C1—O1 = 1.2380(16) Å and C1—N2 = 1.3334(17) Å.

The molecular packing of (I) is dominated by conventional hydrogen bonding which leads to a three-dimensional architecture. A supramolecular tape is formed through the agency of amide-N—H···O(carbonyl) hydrogen bonds [N2—H3n···$O1^{ii}$: H3n···$O1^{ii}$ = 2.013(10) Å, N2···$O1^{ii}$ = 2.8802(13) Å, angle at H3n = 170.1(13)° for (ii) x, $-1 + y$, z]. These are connected into a supramolecular layer parallel to (−1 0 2) by hydrazide-N—H···N(hydrazide) hydrogen bonds [N1—H2n···$N1^{iii}$: H2n···$N1^{iii}$ = 2.303(15) Å, N1···$N1^{iii}$ = 3.1402(15) Å with angle at H2n = 157.8(13)° for (iii) $-x$, $1/2 + y$, $1/2 - z$]. The layers thus formed are connected along the c-axis by hydrazide-N—H···O(carbonyl) interactions [N1—H1n···$O1^{iv}$: H1n···$O1^{iv}$ = 2.397(15) Å, N1···$O1^{iv}$ = 3.2058(14) Å with angle at H1n = 151.5(13)° for (iv) x, $3/2 - y$, $-1/2 + z$], indicating the carbonyl-O1 atom accepts two hydrogen bonds.

A further analysis of the Hirshfeld surfaces and two-dimensional fingerprint plots (overall and decomposed) was conducted in order to ascertain the influence of non-hydrogen bonding contacts upon the molecular packing. Calculations were performed using Crystal Explorer 17 [8] and standard procedures [9]. While O···H/H···O [25.0%] and N···H/H···N [13.0%] make significant percentage contributions to the calculated Hirshfeld surface, H···H contacts dominate, contributing 58.6% of all contacts. The only other contribution to the surface contacts >1% is from C···H/H···C contacts [2.2%].

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